PATENT ABSTRACTS OF JAPAN

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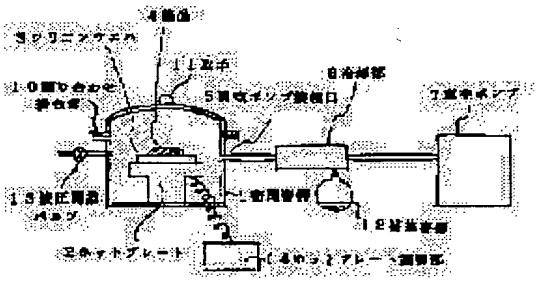
(54) METHOD FOR CHEMICAL ANALYSIS AND EQUIPMENT FOR PRETREATMENT THEREFOR

(57)Abstract:

PURPOSE: To condense a chemical by a quick, simple and safe pretreatment operation and thereby to enable execution of an analysis with high accuracy, by a method wherein after the chemical put on the surface of a wafer is evaporated by heating, a very small quantity of recovery solution containing fluoric acid is dropped onto the surface of the wafer, scanning is made thereon and an evaporation residue is recovered.

CONSTITUTION: The pressure inside a closed vessel 1 is reduced by a vacuum pump 7 and a silicon wafer 3 is heated by a hot plate 2 to condense a chemical 4 by evaporation. Then, a very small quantity of recovery solution containing 77 fluoric acid is dropped onto the surface of the wafer 3, scanning is made all over the surface of the wafer 3 so as to dissolve and recover an evaporation residue, and impurities in the recovery solution are analyzed. Since the surface of the wafer 3 has a high water repellency, according to this method, the dropped recovery solution gathers like balls and moves smoothly on the surface of the wafer 3, and since the recovery solution also has a high solubility, the whole quantity of the evaporation residue can be recovered even by a very small quantity thereof. Thus, condensation of a high multiplication rate can be attained even when the quantity of the chemical to be condensed is small. By executing the condensation under the reduced pressure by using the wafer 3, accordingly, even a high-boiling chemical such as a sulfuric acid can be condensed quickly at a relatively low temperature and an analysis with high sensitivity can be performed.



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CLAIMS

[Claim(s)]

[Claim 1] A silicon wafer which has a clean surface is installed into a decompressed well-closed container, heating evaporation of the chemical put on the surface of this wafer is carried out, and evaporated residue is collected after that by carrying out slight amount dropping of the recovery liquid which contains fluoric acid on this wafer surface, and scanning the wafer surface without a corner. Chemical analytical method characterized by analyzing an impurity in a chemical by analyzing this recovery liquid.

[Claim 2] Chemical analytical method according to claim 1 characterized by heating a chemical at an infrared heater installed above a silicon wafer.

[Claim 3] It is the pretreatment system for drug assays which it is the pretreatment system for drug assays which has a well-closed container, and a vacuum pump and a heating control section, a heater for heating a silicon wafer and a silicon wafer for a well-closed container carrying a chemical is installed in the interior, and a vacuum pump is connected to said well-closed container through the cooling section, and is characterized by a heating control section being what controls temperature control of a heater.

[Claim 4] It is the pretreatment system for drug assays which it is the pretreatment system for drug assays which has a well-closed container, a vacuum pump and an infrared heater, and a heating control section, and a silicon wafer for a well-closed container to carry a chemical and a silicon wafer frame-common-equipment base are installed in the interior, a vacuum pump is connected to the well-closed container concerned through the cooling section, and an infrared heater is installed above a silicon wafer, and is characterized by a heating control section being what controls temperature control of said heater.

[Claim 5] A pretreatment system for drug assays given in claims 3 and 4 characterized by having an uptake container for carrying out uptake of the chemical solidified with a cooling pipe and a cooling

pipe inside a well-closed container.

[Claim 6] A pretreatment system for drug assays according to claim 5 characterized by consisting of cooling pipes which have structure which a solidified chemical concentrates and trickles into one point.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the pretreatment system for the analysis method of the impurity in high **** chemicals, such as a chemical, especially a sulfuric acid, and analysis.
[0002]
[Description of the Prior Art] High grade-ization of the material used in a manufacture process is becoming important with high integration of LSI. In order that the purity of the chemical used at a wafer washing production process may influence the final cleanliness of a wafer, to be especially a high grade is demanded. For example, in the case of a metal impurity, it is necessary to hold down to 1ppb or 0.1ppb or less with the chemical used by manufacture of a future super-high accumulation device. For that purpose, the analysis method of the chemical which can analyze the impurity below such concentration is needed.
[0003] Although analyzed by high sensitivity analysis apparatus, such as atomic absorption and ICP-MS, the impurity in a chemical is difficult for introducing into direct-method-of-analysis equipment under the effect of a matrix, and after pretreatment actuation removes a matrix component, it is analyzed. Conventionally, generally the method of putting a chemical into the container of Teflon or a quartz, heating a chemical, and carrying out evaporation concentration as a pretreating method, is used. About high **** chemicals, such as a sulfuric acid, in order to, aim at low-temperature-izing and the improvement in a vapor rate in evaporation temperature for example, as indicated by JP,62-041703,A, the pretreatment system and analysis method which carry out heating concentration under reduced pressure are used.
[0004] As shown in drawing 6 , after the conventional pretreatment system consisted of reduced pressure openings 25 which are end connections to the thickener tank 21 into which the sulfuric acid 20 was put, heating apparatus 22, the cooling section 23, a receiver tank 24, and a vacuum pump, can perform now evaporation concentration of a sulfuric acid 20 within the decompressed thickener tank 21 and collected the residue in the thickener tank 21 after evaporation concentration with recovery liquid, it was analyzing the impurity in recovery liquid by said analysis apparatus.
[0005]
[Problem(s) to be Solved by the Invention] There were the following

troubles in the conventional technology. That is, with the quality of the materials (a quartz, Teflon, etc.) of the concentration container of 1 former, or a thickener tank, since recovery liquid spreads, in order to improve recovery of evaporated residue, the recovery liquid of a large quantity (about several ml) was comparatively required, and in order to condense a high scale factor, the chemical of a large quantity (about 100ml) needed to be condensed. As a result, concentration took long duration and the possibility of the contamination from an ambient atmosphere etc. was high at the meantime.

2) Like the concentration equipment of drawing 6 , by the method which heats a thickener tank with heating apparatus, there was a danger that the heated chemical would bump, and in order to prevent it, equipment, such as using a thickener tank rotating type distillation apparatus, was complicated, and it had enlarged. Moreover, since the sulfuric acid which evaporated solidifies and returned by the thickener tank portion and the pipe line which are not in contact with heating apparatus, the whole needed to be made into the elevated temperature while covering the portion concerned with heat insulating material. For this reason, it not only requires long duration, but the handling of equipment became complicated and the safety top had a problem in cooling of the equipment after evaporation concentration.

[0006] The purpose of this invention was made in order to solve the conventional technical problem described above, and quickness and offering the chemical analysis method which analysis can perform to high sensitivity simple and safely, and the pretreatment system for drug assays have pretreatment actuation.

[0007]

[Means for Solving the Problem] The chemical analysis method which starts this invention in order to attain said purpose installs a silicon wafer which has a clean surface into a decompressed well-closed container, carries out the heating evaporation of the chemical put on the surface of this wafer, collects evaporated residue by carrying out slight amount dropping of the recovery liquid which contains fluoric acid on this wafer surface after that, and scanning the wafer surface without a corner, and analyzes the impurity in a chemical by analyzing this recovery liquid.

[0008] Moreover, a chemical is heated at an infrared heater installed above a silicon wafer.

[0009] Moreover, a pretreatment system for drug assays concerning this invention is a pretreatment system for drug assays which has a well-closed container, and a vacuum pump and a heating control section, a heater for heating a silicon wafer and a silicon wafer for a well-closed container carrying a chemical is installed in the interior, a vacuum pump is connected to said well-closed container through the cooling section, and a heating control section controls temperature control of a heater.

[0010] Moreover, a pretreatment system for drug assays concerning this invention is a pretreatment system for drug assays which has a well-closed container, a vacuum pump and an infrared heater, and a heating control section, a silicon wafer for a well-closed container to carry a chemical and a silicon wafer frame-common-equipment base

are installed in the interior, a vacuum pump is connected to the well-closed container concerned through the cooling section, an infrared heater is installed above a silicon wafer, and a heating control section controls temperature control of said heater.
[0011] Moreover, it has an uptake container for carrying out uptake of the chemical solidified with a cooling pipe and a cooling pipe inside a well-closed container.
[0012]
[Function] The silicon wafer surface has high water repellence, and the recovery liquid containing the fluoric acid dropped at this surface becomes hard spherically, and moves the silicon wafer surface by the condition of having solidified, smoothly. Moreover, recovery liquid has the high solubility of evaporated residue, and high recovery is acquired. Therefore, if recovery liquid is dropped at the silicon wafer surface and scanned without a corner, evaporated residue can carry out whole-quantity recovery of the amount of the recovery liquid also in a slight amount. For this reason, the amount of the chemical to condense can condense a high scale factor at least.
[0013] If the silicon wafer which has a clean surface is used for a concentration container and it condenses under reduced pressure, since concentration comparatively quick at low temperature is possible and contamination also decreases from an ambient atmosphere etc. also with high **** chemicals, such as a sulfuric acid, high sensitivity can be analyzed. Moreover, the whole equipment does not become an elevated temperature in order for what is necessary just to be to heat the chemical on a silicon wafer or the surface of a wafer. When a chemical is heated at an infrared heater from the upper part, there is no danger of carrying out non-boiling evaporation and bumping.
[0014]
[Example] Next, this invention is explained with reference to a drawing.
[0015] (Example 1) Drawing 1 and drawing 2 are drawings showing the example 1 of this invention. A silicon wafer 3 is carried on the hot plate 2 installed in the interior of a well-closed container 1 in drawing, and the chemical 4 of a constant rate is carried on the surface of a wafer 3. The well-closed container 1 is connected with the vacuum pump 7 through the cooling section 6 by the vacuum pump end connection 5.
[0016] A vacuum pump 7 is operated, the well-closed container 1 interior is made reduced pressure, a silicon wafer 3 is heated with a hot plate 2, and evaporation concentration of the chemical 4 is carried out.
[0017] After evaporation to dryness, as shown in drawing 2 , a slight quantity of recovery liquid 8 is dropped on the surface of a silicon wafer 3, it scans without a corner by the locus as shows a wafer surface top as a continuous line, evaporated residue 9 is dissolved and collected, and the impurity in recovery liquid 8 is analyzed by the analysis apparatus.
[0018] In order that a well-closed container 1 may raise operability, it is made to print mutually, and it can be separated now up and down by the joint 10. The upper part has the structure of a convex up so

that the chemical solidified by the internal surface may not trickle into the surface of a silicon wafer 3, and it has Toride 11 so that it may be easy to work. Between the vacuum pump end connection 5 and the vacuum pump 7, the cooling section 6 and the uptake container 12 for carrying out cooling uptake of the chemical steam are installed. When returning the inside of the decompressed equipment to an atmospheric pressure, the reduced pressure disconnection bulb 13 prepared in the well-closed container 1 is opened. The temperature of a hot plate 2 is controlled by the hot plate control section 14.

[0019] In addition, a fluoric acid solution is used for recovery liquid 8, it is sufficient concentration (for example, 0.5% or more) to dissolve the oxide film generated on the silicon wafer 3 surface in process of pretreatment, and the concentration of fluoric acid should just be within the limits of the concentration (for example, 5% or less) of the degree which does not become a problem by analysis of an analysis apparatus. Moreover, in analyzing an element more precious than silicon, such as gold, silver, and copper, it uses for fluoric acid the recovery liquid which added oxidizers, such as a hydrogen peroxide.

[0020] Evaporation concentration of the sulfuric acid is carried out with the pretreatment system of drawing 1 , and an example of the result when analyzing a metal impurity with the analysis method of this invention is shown below.

[0021] The 10ml sulfuric acid was carried on the 6 inch silicon wafer, and when it condensed on condition that the temperature of about 200 degrees C of a hot plate, and about 20 degree of vacuum Torr(s), concentration was completed in about 10 minutes. The detection lower limit after using 0.2ml of fluoric acid for recovery liquid 5% and collecting evaporated residue (50 times as many concentration rate as this), in case the analytical element of analysis sensitivity when black-smoke furnace atomic absorption equipment analyzes a metal impurity is iron was 0.01ppb.

[0022] In order to obtain the analysis sensitivity of a minimum-limit-of-detection value 0.01ppb degree by the conventional vacuum concentration method, about 100ml of sulfuric acids needed to be condensed. According to the analysis method of this invention, the amount of concentration of a chemical was good at about 1/10, and has also shortened concentration time amount about single figure. Moreover, being heated was limited to the silicon wafer 3, and since it was local, device operation nature, workability, and its safety improved remarkably.

[0023] (Example 2) Drawing 3 is the cross section showing the well-closed container portion of the pretreatment system concerning the example 2 of this invention. The difference from the pretreatment system shown in drawing 1 puts a silicon wafer 3 on the wafer stand 15, and uses the infrared heater 16 formed on the silicon wafer 3 as a source of heating instead of the hot plate 2. Moreover, the control section 17 which controls the infrared heater 16 is installed.

[0024] With the equipment of drawing 1 , since a chemical 4 was heated through a silicon wafer 3, it might bump, but with the equipment of drawing 3 , since it evaporated by the so-called non-boiling evaporation which a chemical is heated at the infrared heater 16 and

evaporates gradually from the surface, bumping was able to be suppressed. By adjusting the reinforcement of the infrared heater 16, the same engine performance as the case of an example 1 has been attained.

[0025] Although the infrared heater 16 is incorporated in the well-closed container 1 with the equipment of drawing 3 , as long as sufficient heating engine performance is obtained by the improvement of the structure of a well-closed container 1 etc., it may be installed out of a well-closed container 1 in consideration of handling nature. Moreover, as for a configuration, magnitude, and an installation location, what can heat only the chemical 4 on a silicon wafer 3 efficiently is good.

[0026] (Example 3) The cross section which looked at the pretreatment system which drawing 4 requires for the example 3 of this invention from the side, and drawing 5 are the cross sections seen from the transverse plane. As compared with the pretreatment system shown in drawing 3 , the cooling pipe 18 and the uptake container 19 for carrying out cooling uptake of the chemical steam are installed in the well-closed container 1.

[0027] A cooling pipe 18 is installed between two infrared heaters 16, and has the structure where cooling water can be poured. Moreover, the solidified chemical has prevented being dropped at the silicon wafer 3 surface by having the structure of a convex lucky, dropping the chemical solidified with the cooling pipe 19 from a lower limit, and making it the configuration by which uptake is carried out with the uptake container 19 prepared downward.

[0028] The chemical steam generated on the silicon wafer 3 flows in in the direction of the vacuum pump end connection 5. Therefore, in order to gather the collection efficiency of a chemical steam, as for the installation location of a cooling pipe 18, it is desirable that it is in the middle of the top in the middle of the direction where a chemical steam flows (i.e., the line which connects the vacuum pump end connection 5 to a silicon wafer 3). In consideration of this, the vacuum pump end connection 5 is formed in the location which the chemical which is the upper part of a well-closed container 1, and was solidified in near does not trickle into a silicon wafer 3 with the equipment of drawing 4 .

[0029] Although operability worsened in the pretreatment system of an example 1 or an example 2 since the chemical steam which evaporated from the silicon wafer 4 surface condenses and adhered in well-closed container 1 inside, this problem was solved by making it the structure shown in the pretreatment system of an example 3.

[0030]

[Effect of the Invention] As explained above, according to the chemical analysis method and the pretreatment system for drug assays of this invention, as compared with the conventional vacuum concentration method, the enrichment of a chemical is good at about 1/10, and can shorten concentration time amount about single figure. Moreover, it is limited to the chemical on a silicon wafer or the surface of a wafer, and since it is local, heating can improve device operation nature, workability, and safety remarkably. Moreover, in order to carry out non-boiling evaporation using an infrared heater,

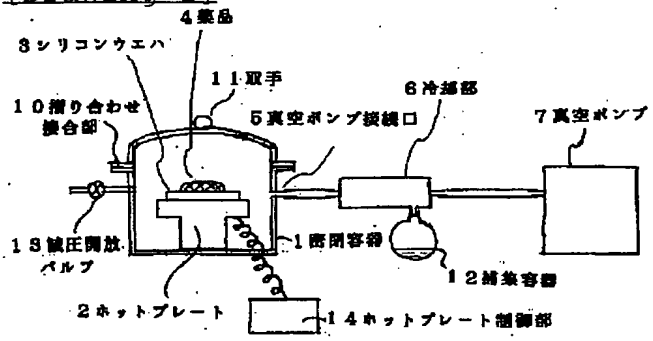
there is also no danger that a chemical will bump, an equipment configuration can be simplified, and workability can be improved.

DESCRIPTION OF DRAWINGS

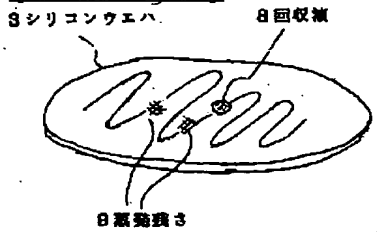
[Brief Description of the Drawings]
[Drawing 1] It is the cross section showing the pretreatment system concerning the example 1 of this invention.
[Drawing 2] It is drawing showing the condition on a silicon wafer.
[Drawing 3] It is the cross section showing the pretreatment system concerning the example 2 of this invention.
[Drawing 4] It is the side cross section showing the pretreatment system concerning the example 3 of this invention.
[Drawing 5] It is the transverse-plane cross section showing one configuration of the pretreatment system concerning the example 3 of this invention.
[Drawing 6] It is the cross section showing the configuration of the pretreatment system concerning the conventional example.
[Description of Notations]
1 Well-closed Container
2 Hot Plate
3 Silicon Wafer
4 Chemical
5 Vacuum Pump End Connection
6 Cooling Section
7 Vacuum Pump
8 Recovery Liquid
9 Evaporated Residue
10 You Make it Print Each Other and it is Joint.
11 Toride
12 Uptake Container
13 Reduced Pressure Disconnection Bulb
14 Hot Plate Control Section
15 Wafer Stand
16 Infrared Heater
17 Control Section
18 Cooling Pipe
19 Uptake Container

DRAWINGS

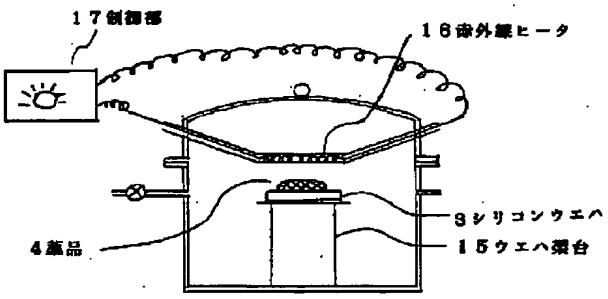
[Drawing 1]



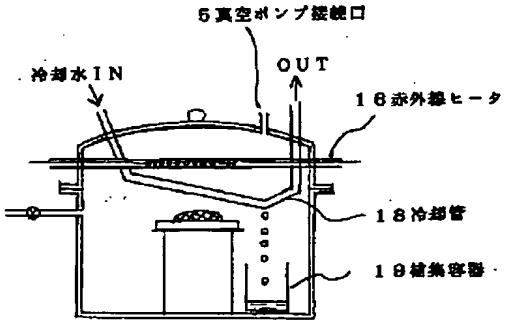
[Drawing 2]



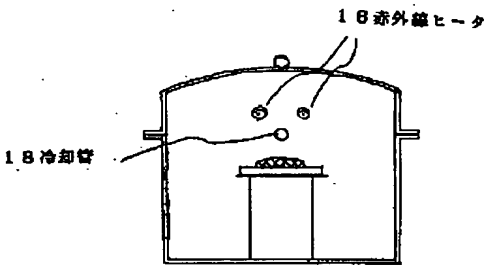
[Drawing 3]



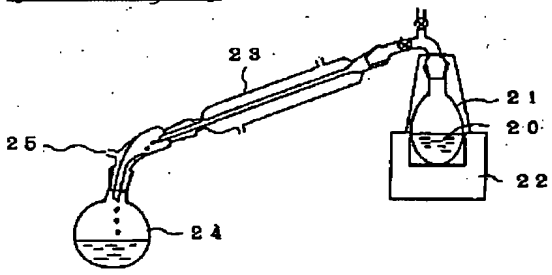
[Drawing 4]



[Drawing 5]



[Drawing 6]



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